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CLEANING OF HARD SURFACE

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ABSTRACT

PURPOSE: To prevent the occurrence of new contamination by a method wherein ultraviolet light is irradiated on the hard surface, whereon organic foreign substances exist, of a matter be cleansed before the matter to be cleansed is cleansed with a cleaning fluid.

CONSTITUTION: In case the hard surface, whereon organic foreign substances exist, of a matter to be cleansed is dried after being cleansed with a cleaning fluid, ultraviolet light is irradiated on the hard surface before the cleaning. That is, by irradiating the ultraviolet light on the matter to be cleansed before the matter to be cleansed is cleansed with the cleaning fluid, the organic foreign substances of a photo resist and so on remaining on the surface of the matter to be cleansed are subjected to chemical change, are decomposed and disappeared on the spot and are brought in a state that they are easy to dissolve or peel with the cleaning fluid in a cleaning treatment to be executed with a cleaning fluid subsequent to that. Thereby, it is eliminated that organic foreign substances remain on the surface of the matter to be cleansed after the matter to be cleansed is subjected to cleaning treatment with a cleaning fluid and the occurrence of new contamination can be prevented.

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政発明の名称 硬表面の洗浄方法

②特 顧 昭62-106069

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1. 発明の名称

要表面の洗浄方法

2. 特許請求の範囲

存成系異物が存在する疑衷面を洗浄液により洗 作した後に乾燥する洗浄方法において、前記洗浄 旅による抗争の任意の工程の前に前記を表面に常 外線を照引する工程を設けたことを特徴とする優 裏面の洗浄方法。

3. 発明の詳細な説明

[産衆上の利用分野]

本定明は硬表面の洗浄方法に係り、詳しくは、 例えば半導体プロセスにおいてフォトマスクブラ ンクやフォトマスク、あるいは半導体基板等を洗 かする 都合に用いられる 雄式 表帯方法に関する。

〔従来の技術〕

従来この柱の遊式洗浄方法としては、一般に、 被洗浄物を少なくとも2種以上の洗浄線(例えば 硫酸、純水、アルコール等)に取次改数し、必要 に応じて抗浄液中に超音波を伝見させて抗浄処理 した頃、アルコール等の蒸気により気が疲を気化 し松豊する方法が知られている。

【発明が解決しようとする問題点】

しかしながら、上記した母式佐彦方法により被 洗浄物を洗浄処理した場合、洗浄処理したにも利 らず、洗炸処理機の独洗が物に汚れの存在が続め られる。その原因として、被抗抑制上に因むして いる残骸レグスト等の存業系異物が上記佐作虹点 によって完全には数去されずに洗浄処理後も被洗 作物上に一部残留することが挙げられる。また他 の原因として、被抗浄物上に囚者している税包レ ジスト等の存機系異物が洗浄処理に用いられる数 論證等の洗浄機と化学反応して被洗浄物の表面に 新たな反応生成物として沈着することが挙げられ る。さらにもう1つの原因として、洗が処理にお いて用いられる異なる種類の洗浄波の化学反応に より、被洗浄物の表面に新たな反応生成物が生じ ることが挙げられる。この異なる種類の洗浄液剤 恋の七季反応による汚れの死生について更になり 的に述べると、この種の被洗浄物の洗浄処理には、 上述の知く従来の母式洗浄方法では、被洗浄物の表面に囚者している有機系典物からなる汚れを完全に除去することは国質であり、この有機系典物と洗浄液との反応、洗浄液周志の反応により新たな汚れが被洗浄物の表面に発生するという問題にがあった。

物が残留することがない。

また常外線阻倒処理によって前記の有機系異物は抗浄液による抗浄処理的に被抗浄物の表面上に最早存在していないので、有機系異物と洗浄液との化学反応により新たな反応生成物が被洗浄物液質上に形成沈低することもない。

本のでは、 のでは、 のでは

【実施術】

本党明は、こ ような関節点を解決するために なされたものであり、その目的は、被洗浄物の表 面に囚打した存職系費物からなる時れを完全に除 去し得ると共に洗浄処理に作う新たな時れの発生 のない洗浄方法を契例することにある。

【問題点を解決するための手段】

水発剤は、上記目的を達成させるためになされたものであり、有機系異物が存在する硬表面を洗浄数により携帯した後に乾燥する洗浄方法において、前記洗浄波による洗浄の任意の工程の質に前記便表面に紫外線を限削する工程を設けたことを動物とするものである。

【作用】

佐浄旅による洗浄前に被洗浄物に無外線を照明することにより、被洗浄物の表面に残留しているフォトレジスト等の有間系具物が化学変化を受け、その幅で分解質失したり、その板の洗浄板による洗浄処理において洗浄波によって溶解又は剥解しやすい状態になるので、被洗浄物の洗浄液による洗浄処理機に被洗浄物の表面上に前記の有機系異

被洗浄物の設盤洗浄、純水洗浄及びイソプロピルアルコール(以下「PAと略称する)洗浄を取次行なった番。被洗浄物を「PA裁弦を用いて乾燥する提来のフォトマスク洗浄方法において、繊維洗浄的に被洗浄物を紫外枠照射処理する安施例について以下に製明する。

被吹作物として、周知のレジストエ包で、エッチングエ程をよびフォトレジスト別能工程を建たであるトマスクを用いた。すなわち、被洗や物であるフォトマスクは、透光性ガラス基を介である。光性機を被殺してなるトマスストである。のは、ボジウンを対して対し、所がなっとなって、カーンをマストに対して、変化を対したものである。

このフォトマスク(大きさ5×5×0.09インチ)4枚を、低圧水銀灯を具備してなる無外箱 型射装置(処理室容析:3240cm³)内に配置 し、常外数風朝処理を行なった。

処理条件は、以下の通りである。

京外的館… 2 5 3 7 人の豚科の強症が全体の 9 0 %、 1 8 4 9 人の舞蹈の強症が 全体の取%である低圧水銀灯を用い た。

低圧水型灯に供給する物パワー・770W ウェットエアー・・ 紫外線限的装置のガス導入口 から301/分の装造で導入した。 ウェットエアーは紫外線限制時に 03 の発生効率を向上させる作用を する。

犯理時間…5分

無外的照例処理機の被洗浄物を次いで洗浄処理し、化燥処理した。すなわち、洗浄処理は、被洗浄物を製度98%の要減機1種に5分間要請し、次に純水1種に30秒間提派し、更にIPA1種に3分間要領することにより行なった。なお被洗浄物のIPA種提供に取しては、IPA被中に設立数(45kHz と46kHz の周数数を交互に維

かつ 洗浄 虹道 時間 の 化学 反応 に 伴う 新 たな 反応 生 成 物 の 発生 もない の で 、 洗浄 虹 理 機 の 被 洗浄 物 の 指 掛 性 が 十 分 に 程 径 さ れ る こ と が 明 ら か で あ る 。

上の実施例では被洗作物として、ポジ型(光分解型)フォトレジストが残留囚着しているフォトマスクを用いたが、本発明の方法においてはネガ型(光優化型)フォトレジストが残稽囚着している 液洗浄物を洗浄処理するこもでき、またレジストがポジ型及びネガ型電子線レジストであっても 同様である。

また本知明の方はは、フォトマスクの洗浄に離 足されるものではなく、フォトマスクプランク、 ガラスは板、透明準電説付きガラス基板、シリコ ンウェハ等、更にはカメラレンズ等の光学レンズ や吸収レンズを被洗浄物とし、これらの表面に付 着乃至固着している有機系異物(例えば大気中の ごみに山米する汚染物や手指接触による汚染物等) を除去するためにも用いられる。

また紫外線原射条件は、被洗浄物の材質及び洗 作処理前に経てきた工程等により適宜選定しうる。 り難し見生する発掘器を使用した。パワーは400Wである。)を伝戴して超音放洗浄を行なった。 兼配 洗浄処型協の乾燥処理は1PA給から引き上げられた複洗浄物を1PA意気には許するこ

上記の卸く業外線限制処理被に洗浄、 乾燥処理された被洗浄物 1 6 枚について、 その様か化の収合を収集したが、 1 6 枚ともに汚れが認められなかった。

とにより行なった。

なお、常外線取引型更を行なわずに同様の抗作、 乾燥処理を行なった被洗浄物15枚についても同様にその富浄化の収合を収取したが、15枚とも に全面に汚れが認められた。また洗浄処理におい て美水便器洗浄処理を3階とし、各特提費時間を それぞれ100秒としても、無外線を照引しない 場合には被洗浄物の全面に汚れが認められること が多々あった。

この支給例の結果から、無外勢限例処理を行な う本発明の方法によれば、被洗浄物表面上に固む している有機系集物が効果的に飲去されており、

すなわち、常外職を照例する光面として、水根ア - クランプ、中圧水製ランプ、高圧水銀ランプ、 キセノンランプ、塩水ランプ界を用いてもよく、 また導入ガスとして、上の実施例で用いたウェッ トエアーの代りにドライエアーやオゾン (〇、) 等を使用しても良く、さらにパワー、処理時間等 も任意に変動させることができる。また触来もの ガスを含有する雰囲気中で紫外値を煎射しても良 く、この場合には観察が集外線照例時にオゾンに なって、被抗か物上に付着している時れ成分の酸 化分解等が促進される。またアルゴン、拡展者の 不抵性ガスを含有する雰囲気中で無外線を取引し ても良い。取引する衆外腺の故及は上の実施例に 記したもの以外に任意の故臣であってよいが、有 概象等の異物を効果的に減少・原去せしめるため には1000~3000人の放展を存する紫外線 を照射することが望ましい。

また上の支施例では、緩破失作に先立って紫外 糖型射動型を行なったが、木丸前の方法において、 紫外数数射動理時間はこれに限定されるものでは なく、 保証洗浄後で 能水洗浄的または 純水洗浄後で 「 PA洗浄的に 無外線照射処理を実施して も良く、 また 削えば 硫酸洗浄的及び硫酸洗浄板で 純水 洗浄的の 如く 無外線照射 処理を 2 回以上行なって も良い。

もちろん被抗疗物の抗挣披中への浸漉洗浄に際

スク、フォトマスクブランク、ガラス基板、半導体基板等、更には光学レンズや職談レンズ等の硬表面を有する物品を効果的に積か化することを実現するものであり、その工業的産業は極めて多大で4.5

特許出順人 ホーヤ 株 式 会 社 代理人 弁理士 中 村 節 男 して、鉄路被印に超高波を伝鞭させたり、あるい は被洗浄物を延動させたりすることは任意である。

また氏が処理として、上述の被抗が物を抗作被中に改設する方法の代りにスピンナー等で被抗作物を回転させながら決が被をスプレーする方法や 被抗が物に加圧(存在ジェット化)された洗浄被 を助きつける方法などを試用することもできる。

上の実施例では被抗事物の乾燥処理として、 1 P A 磁気による磁気を離せ採用したが、 フロンギの他の温気を用いる温気を見でも良く、またスピンを嫌でも良い。

本見明の方法は、紫外線照射型更を行なわない 造常の携帯方法を実施した結果、異なる砂質の洗 浄波(例えば硫酸とアルコール)の化学反応によ る汚れが発生した被洗浄物の再洗浄のためにも行 焼であり、紫外線照射処理提に洗浄線による可洗 浄処理を行なうことによって、造常の条件では除 去個数な汚れを除去することが可能である。

[発明の効果]

以上非親したように、木兒明の方法はフォトマ

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SPECIFICATION

1. Title of the Invention: METHOD FOR CLEANING HARD SURFACE

2. Claim

A method for cleaning a hard surface having organic foreign substances, comprising cleaning the hard surface with a cleaning solution, followed by drying, wherein a step of irradiating the hard surface with ultraviolet light is provided before any given step of cleaning with the cleaning solution.

Detailed Description of the Invention [Industrial Field of the Invention]

The present invention relates to a method for cleaning a hard surface, and more particularly relates to a wet cleaning method which is used, for example, when a photomask blank, a photomask, a semiconductor substrate, or the like

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is cl aned in a semiconductor process.

[Description of the Related Art]

The known wet cleaning method generally includes the steps of cleaning by immersing a workpiece to be cleaned in at least two cleaning solutions (e.g., sulfuric acid, pure water, and alcohol) one after another, and as required, by propagating ultrasonic waves into the cleaning solutions, and then drying by vaporizing the cleaning solutions by means of vapors of alcohol or the like.

[Problems to be Solved by the Invention]

However, when a workpiece is subjected to cleaning treatment by the wet cleaning method described above, the workpiece after cleaning is observed to have contamination in spite of the cleaning treatment. One of the reasons for this is that organic foreign substances such as a residual resist stuck on the workpiece are not completely removed by the cleaning treatment and partially remain on the workpiece after the cleaning treatment. Another reason is that organic foreign substances such as a residual resist stuck on the workpiece chemically react with a cleaning solution such as concentrated sulfuric acid, and a new reaction product is deposited on the surface of the workpiece. Still another reason is that different types of cleaning solutions used in the cleaning treatment chemically react with each other, and a new reaction product is generated on the

surface of the workpiece. The g neration of contamination due to th chemical reaction between the different types of cleaning solutions will be further described in d tail. In order to clean this type of workpiece, for example, cleaning treatment in which concentrated sulfuric acid immersion cleaning and alcohol immersion cleaning are combined is employed. In this cleaning treatment, after concentrated sulfuric acid immersion cleaning is performed in one vessel, pure water immersion cleaning is performed in three vessels b fore alcohol immersion cleaning in one vessel. Even if such pure water cleaning treatment is intervened, when foreign substances or the like exist on the surface of the workpiece or surface wettability of the workpiece is not uniform, sulfuric acid sticks and remains on the surface of the workpiece after pure water treatment and reacts with alcohol in the subsequent alcohol immersion cleaning. treatment to generate a kind of esterified reaction product. In such a case, it is difficult to remove contamination due to the reaction product even by cleaning again with a cleaning solution such as sulfuric acid or alcohol, which is particularly troublesome.

As described above, in the known wet cleaning method, it is difficult to completely remove contamination due to organic foreign substances stuck on the workpiece, and new contamination may occur on the surface of the workpiece

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because f a reaction between the organic foreign substances and a claning solution or a reaction between the individual claning solutions.

The present invention overcomes the foregoing problems. It is an object of the present invention to provide a method for cleaning in which contamination due to organic foreign substances stuck on the surface of a workpiece can be completely removed and new contamination associated with cleaning treatment can be prevented.

[Means for Solving the Problems]

The present invention was made to achieve the object described above, and in a method for cleaning a hard surface having organic foreign substances with a cleaning solution, followed by drying, a step of irradiating the hard surface with ultraviolet light is provided before any given step of cleaning with the cleaning solution.

[Operation]

By irradiating a workpiece with ultraviolet light before cleaning with a cleaning solution, organic foreign substances such as a photoresist that remain on the surface of the workpiece are subjected to a chemical reaction, and the organic foreign substances may be decomposed and disappear at that stage or may become to be easily dissolved or removed by a cleaning solution in the subsequent cleaning treatment with the cleaning solution. Therefore, the

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organic f reign substances do not remain on the surface of the workpi ce after the cleaning treatment with the cleaning soluti n.

Additionally, by the ultraviolet radiation treatment, since the organic foreign substances do not exist on the surface of the workpiece any more during cleaning treatment, a new reaction product is not generated due to a chemical reaction between the organic foreign substances and the cleaning solution.

Moreover, since surface wettability of the workpiece is improved by the ultraviolet radiation treatment, the cleaning solution spreads over the surface of the workpiece uniformly, and cleaning treatment with the cleaning solution can be performed uniformly over the entire workpiece, and also draining is easily performed when the workpiece is withdrawn from the cleaning solution and the cleaning solution does not remain partially concentrated on a portion of the surface of the workpiece. Thereby, for example, in a cleaning method in which sulfuric acid immersion cleaning treatment and alcohol immersion cleaning treatment are combined, if a simple pure water immersion cleaning treatment step for eliminating sulfuric acid that remains slightly on the surface of the workpiece is provided between the sulfuric acid treatment and the alcohol treatment, new contamination due to a chemical reaction between sulfuric

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acid and alcohol do s not occur.

[Example]

With resp ct to a conventional m thod for cleaning a photomask in which a workpiece is subjected to sulfuric acid cleaning, pure water cleaning, and isopropyl alcohol (hereinafter abbreviated as IPA) cleaning in that order, followed by drying using IPA vapors, an example in which the workpiece is subjected to ultraviolet radiation treatment before sulfuric acid cleaning will be described below.

As a workpiece, a photomask obtained by the known steps of resist, etching, and photoresist stripping was used. That is, in order to obtain the photomask as a workpiece, AZ-1350 (manufactured by Hoechst) as a positive photoresist was applied on a photomask blank in which a chrome shading film was formed on a transparent glass substrate, exposure and development were performed through a mask having—a predetermined pattern, the shading film was etched using the resist pattern as a mask, and then the resist pattern was stripped.

Four sheets of such a photomask with dimensions of 5 \times 5 \times 0.09 inch were placed in an ultraviolet irradiation system (treatment-chamber volume: 3,240 cm³) and ultraviolet radiation treatment was performed.

Treating conditions are as follows.

Ultraviolet source: low-pressure mercury-vapor lamp,

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in which the intensity of an emission line at 2,537 Å occupies 90% and the intensity of an emission line at 1,849 Å occupies several percents of the total intensity.

Total power applied to low-pressure mercury-vapor lamp:
770 W

Wet air: Introduced at a velocity of 30 1/minute from a gas inlet of the ultraviolet irradiation system. Wet air improves the efficiency of O_3 generation during ultraviolet radiation.

Treating time: 5 minutes

After ultraviolet radiation treatment, the workpiece was subjected to cleaning treatment, followed by drying treatment. That is, cleaning treatment was performed by immersing the workpiece in one-vessel concentrated sulfuric acid having a concentration of 98% for 5 minutes, next by immersing in one-vessel pure water for 30 seconds, and further by immersing in one-vessel IPA for 3 minutes. With respect to the immersion of the workpiece in the IPA vessel, ultrasonic cleaning was performed by propagating ultrasonic waves into the IPA solution. (An ultrasonic oscillator for generating frequencies of 45 kHz and 46 kHz alternately was used. Applied power was 400 W.)

Drying treatment after the cleaning treatment was performed by exposing the workpiece withdrawn from the IPA

v ss 1 to IPA vapors.

With r spect to 16 workpiec s which w re cleaned and dried aft r ultraviolet radiation treatment as described above, the cleanliness level was inspected. Contamination was not observed in all 16 workpieces.

With respect to 15 workpieces which were cleaned and dried in a similar manner without performing ultraviolet radiation treatment, the cleanliness level was inspected. Contamination was observed in the entire surfaces of all 15 workpieces. Even when pure water immersion cleaning treatment was performed in three vessels and the immersion time was set for 100 seconds each, contamination was often observed in the entire surface of the workpiece when ultraviolet radiation was not performed.

As a result of this example, in the method in which ultraviolet radiation treatment is performed in accordance with the present invention, organic foreign substances stuck on the workpieces are effectively removed and a new reaction product associated with a chemical reaction during cleaning treatment is not generated, and thereby it is clear that cleanliness of the workpieces after cleaning treatment can be secured satisfactorily.

Although in the example described above, a photomask stuck with a residual positive (photodegradable) photoresist was used, in the method in accordance with the present

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invention, a workpi c stuck with a residual negative (photo-setting) photoresist may be cl aned, and in the case of positiv and negative electron beam resists, the method also can be used similarly.

The method in accordance with the present invention is not limited to cleaning of photomasks. Photomask blanks, glass substrates, glass substrates provided with transparent conductive films, silicon wafers, and the like, and additionally, optical lenses such as camera lenses and spectacle lenses may be considered as workpieces, and the method is used to remove organic foreign substances (e.g., contaminants due to dust in air or contaminants due to finger contact) attached or stuck to the surfaces thereof.

Ultraviolet radiation conditions may be selected appropriately depending on materials of workpieces and processes undergone before cleaning treatment. That is, as a light source for ultraviolet radiation, a mercury arc lamp, a medium-pressure mercury lamp, a high-pressure mercury lamp, a xenon lamp, a heavy-water lamp, or the like may be used. As an induction gas, instead of wet air used in the example described above, dry air, ozone (O₃), or the like may be used. Moreover, power and treating time may be varied voluntarily. Ultraviolet radiation may be performed in an atmosphere containing a gas such as oxygen, and in such a case, oxygen changes into ozone during ultraviolet radiation

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and oxidative d struction or the like of contaminants stuck on the w rkpiece is accelerated. Ultraviolet radiati n may also be performed in an atmosphere containing an inert gas such as argon or nitrogen. Although ultraviolet light radiated may have a given wavelength in addition to that described in the example, in order to effectively reduce and remove foreign substances such as organic substances, it is desirable that ultraviolet light having a wavelength of 1,000 to 3,000 Å be radiated.

Although ultraviolet radiation treatment was performed before sulfuric acid cleaning in the example described above, the timing of ultraviolet radiation treatment is not limited to this in accordance with the method of the present invention. Ultraviolet radiation treatment may be performed after sulfuric acid cleaning and before pure water cleaning or after pure water cleaning and before IPA cleaning, or ultraviolet radiation treatment may be performed at least twice, for example, before sulfuric acid cleaning, and after sulfuric acid cleaning and before pure water cleaning.

With respect to cleaning treatment after ultraviolet radiation treatment, although sulfuric acid, pure water, and IPA were used in that order in the example described above, cleaning treatment used in the method of the present invention is not limited to this. For example, cleaning treatment using aqueous hydrogen peroxide only, IPA only, or

hydrog n peroxid and IPA may be adopted. In cleaning treatment using aqueous hydrogen p roxide only or IPA only, ultraviolet radiation treatment is performed before cleaning with aqueous hydrogen peroxide or IPA, and in cleaning treatment using aqueous hydrogen peroxide and IPA, ultraviolet radiation treatment is performed at a given stage before aqueous hydrogen peroxide cleaning, after aqueous hydrogen peroxide cleaning, after cleaning, or after pure water cleaning and before IPA cleaning.

Of course, when a workpiece is subjected to immersion cleaning in a cleaning solution, ultrasonic waves may be propagated into the cleaning solution, or the workpiece may be oscillated.

As cleaning treatment, instead of immersing a workpiece in a cleaning solution as described above, a method of spraying a cleaning solution while a workpiece is rotated by a spinner or the like, or a method of spraying a workpiece with a pressurized (high-pressure jet) cleaning solution may be adopted.

With respect to drying treatment of the workpiece, although vapor drying by IPA vapors was adopted in the example described above, vapor drying using other vapors such as flon may be used, or spin drying may be used.

The method of the present invention is also effective

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in r cl aning a workpi ce in which contamination has occurred due to a chemical reaction betw n diff r nt types of cleaning solutions (for xample, sulfuric acid and alcohol) as a result of carrying out a general cleaning process without ultraviolet radiation treatment. By recleaning treatment with a cleaning solution after ultraviolet radiation treatment, contamination that is not removable under normal conditions can be removed.

[Advantages]

As described above in detail, the method in accordance with the present invention makes it possible to effectively clean photomasks, photomask blanks, glass substrates, semiconductor substrates, and the like, and also articles having hard surfaces such as optical lenses and spectacle lenses, and the industrial significance of the invention is great.

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